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In Situ FT-IR Studies of Reactions of Activated Sphalerite With Aqueous Solutions of Potassium Ethylxanthate

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UNITED STATES DEPARTMENT OF THE INTERIOR

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ILLUSTRATIONS

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm	centimeter	mm	millimeter
cm^{-1}	wavenumber unit	µm	micrometer
h	hour	MΩ	megohm
M	molar concentration	mol	mole
min	minute	pct	percent
mL	milliliter		

IN SITU FT-IR STUDIES OF REACTIONS OF ACTIVATED SPHALERITE WITH AQUEOUS SOLUTIONS OF POTASSIUM ETHYLXANTHATE

By S. C. Termes [1] and P. E. Richardson [2]

ABSTRACT

The Bureau of Mines has used Fourier transform infrared spectroscopy (FT-IR) to study in situ reactions of aqueous solutions of potassium ethylxanthate with Cu(II)- and Pb(II)-activated sphalerite plates, in which the plates were both the infrared-transparent windows and the reacting surfaces. A copper (I) ethylxanthate formed predominantly with Cu(II)-activated sphalerite, regardless of the activation time. The products formed on Pb(II)-activated sphalerite depended on the activation times; a short activation time (30 min) yielded a lead ethylxanthate-like product, but a long activation time (90 min) yielded a considerable amount of dixanthogen.

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INTRODUCTION

The Bureau of Mines has been using in situ spectroelectrochemical techniques (ultraviolet and visible regions) to study the reactions of thio collectors with sulfide minerals (1-3) in order to expand the understanding of the physical, chemical, and electrochemical reactions controlling flotation behavior. However, ultraviolet and visible spectroscopy does not provide sufficient unambiguous molecular information to completely characterize the ongoing reactions. For this purpose infrared spectroscopy is required. Owing to the strong absorption of infrared radiation by water, routine studies of in situ reactions in aqueous solutions have been difficult. This limitation imposed by the absorption of water has been partly overcome by the higher energy throughput, higher signal-to-noise ratio, and higher sensitivity of the FT-IR instruments developed in recent years. Studies of electrochemical reactions at the electrode-electrolyte interface using FT-IR have been reported for nonaqueous as well as aqueous electrolytes (4-8). FT-IR has also been employed in leaching studies of chalcopyrite (9).

The authors are currently applying FT-IR spectroscopy to in situ studies of flotation reagent-sulfide mineral interactions. The reaction of activated sphalerite (ZnS) with potassium ethylxanthate, $CH_3CH_2-O-C\lesssim^{S}_{S^-K^+}$, was chosen because it appeared to be an ideal case. Synthetic zinc sulfide (commonly referred to as IRTRAN2) is a well-known infrared-transparent material, as shown in figure 1*A*. Polished plates of natural sphalerites (cubic ZnS), on the other hand, show a strong absorption region between 4,500 and 2,500 cm^{-1} (figs. 1*B*-1*D* and fig. 2). Absorption in this region has been attributed to electronic transitions of

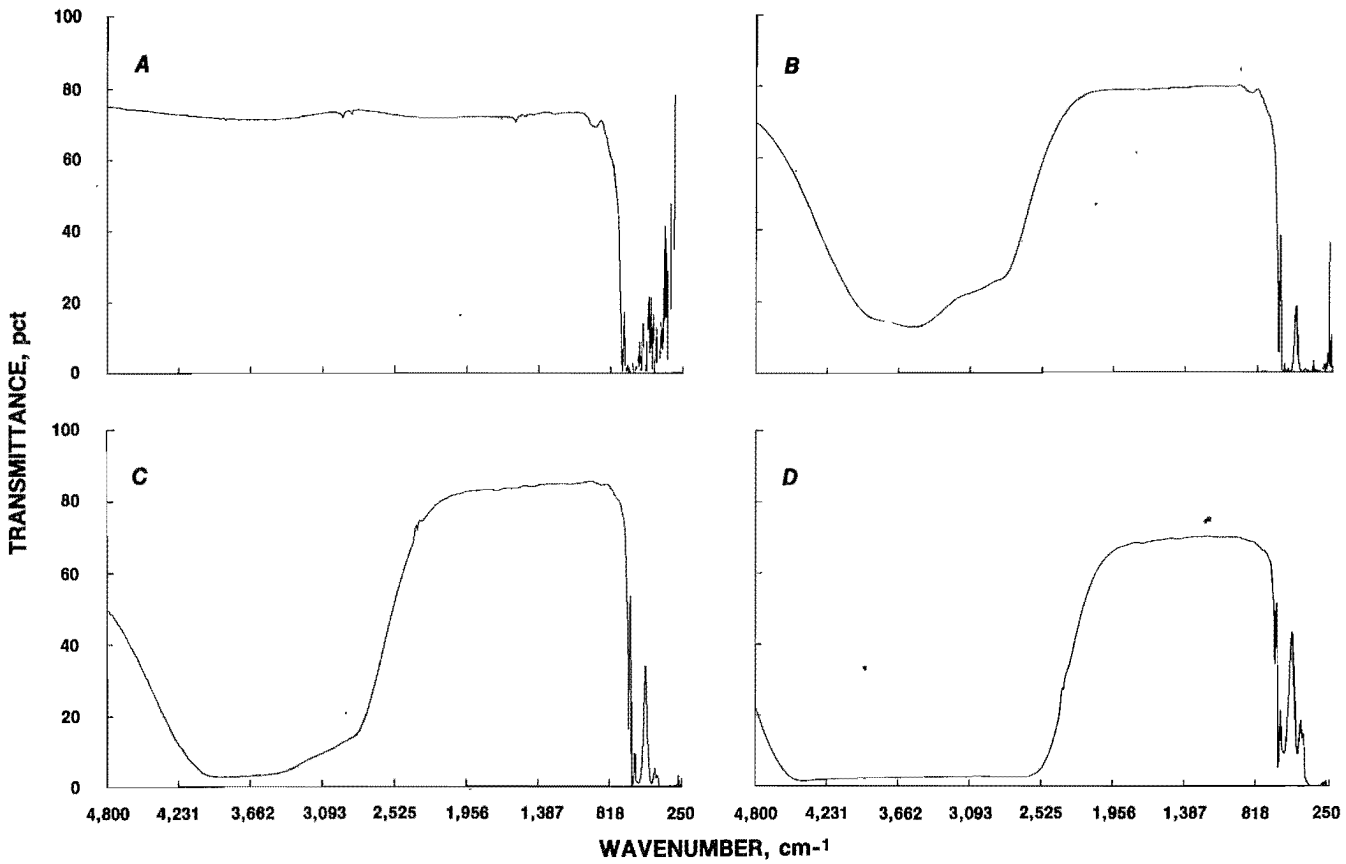


FIGURE 1. - Comparison of the transmission spectra of zinc sulfide from different sources. *A*, Synthetic (IRTRAN2 window); *B*, Santander sphalerite; *C*, Santa Eulalia sphalerite; *D*, Balmat sphalerite.

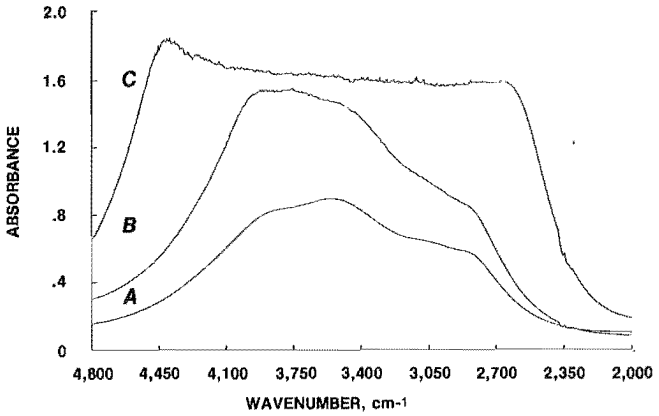


FIGURE 2. - Electronic absorption spectra of Fe(II) in sphalerites from different regions. *A*, Santander; *B*, Santa Eulalia; *C*, Balmat.

Fe(II) (10-11), iron being a common impurity in natural ZnS. (The increase in absorbance as a result of an increase in iron content in natural sphalerites is well illustrated in figure 2.) However, between 1,300 and 900 cm^{-1}, the region where most of the characteristic vibrational absorption bands of xanthates occur, these plates exhibit a convenient window to study xanthate reactions by a simple transmittance technique. Preliminary experiments showed that a high-quality potassium ethylxanthate spectrum in aqueous solution could be obtained from a drop of the solution compressed between two sphalerite plates.

Previous infrared spectroscopic work on dodecylxanthate adsorption on sphalerite by Yamasaki and Usui (12) had used KBr pellet techniques to identify the reaction products. Coleman, Powell, and Cochran (13), although they used sphalerite plates, employed internal reflectance methods, Nujol mulls, and liquid sampling from nonaqueous extracts to study the reaction products on dried surfaces. Infrared spectroscopy studies of xanthate adsorption on lead sulfide (14-17), lead (16), copper (15-16), and nickel (18) have also been reported. However, in situ infrared spectroscopy studies involving mineral-collector reactions in aqueous solutions have not been reported. To explore the possibility of applying FT-IR to this problem, the Bureau of Mines undertook the present work on the reactions of aqueous solutions of potassium ethylxanthate with Cu(II)-activated and Pb(II)-activated sphalerite.

ACKNOWLEDGMENT

The authors express their appreciation to Dr. Alan N. Buckley, senior research scientist, Commonwealth Scientific and Industrial Research Organization (CSIRO), Institute of Energy and Earth Resources, North Ryde, Australia, for the X-ray photoelectron spectroscopic measurements and for helpful discussions while he was visiting the Bureau's Avondale (MD) Research Center on a sabbatical leave from CSIRO.

EXPERIMENTAL WORK

SPECTROSCOPIC MEASUREMENTS

Infrared spectra were taken with a Nicolet 20SX FT-IR[3] spectrometer fitted with a globar source, a cesium iodide beamsplitter, and a deuterium triglycine sulfate (DTGS) detector. This combination of beamsplitter and detector provided a frequency range from 5,000 cm^{-1} down to 225 cm^{-1}. The resolution was set at 2 cm^{-1}. To hold the plates in place in the sample compartment, it was convenient to use a Barnes demountable pathlength cell with sphalerite plates used as the optical windows.

Each spectrum was obtained by collecting 100 interferograms, which were automatically coadded and signal-averaged to produce a high-quality interferogram. Fourier transformation of this interferogram yielded a single-beam spectrum, which was then ratioed against the single-beam background spectrum. Unless otherwise specified, all spectra are presented as absorbance spectra.

[3]Reference to specific products does not imply endorsement by the Bureau of Mines.

SAMPLE PREPARATION

Sphalerite samples from Santander, Spain, Santa Eulalia, Mexico, and Balmat, NY, were purchased from Ward's Natural Science Establishment. No crystallographic evidence for hexagonal ZnS (wurtzite) was found in the samples.

Santander sphalerite samples were monomineralic and contained only traces of Fe, Cu, Pb, and Mn. The Mexican sphalerite showed some chalcopyrite inclusions and traces of Pb, Cd, Ag, and Mn. The Balmat sphalerite contained 5.1 pct Fe, minor amounts (<1 pct) of Pb (as galena), and traces of pyrite and quartz.

Slices of the mineral were cut with a diamond saw from cubes of transparent pieces, which were subsequently ground and polished with a microprocessor-controlled grinding and polishing machine to a final finish with 6-μm diamond paste. The resulting polished plates were washed with acetone and water to remove organic residues.

Plates of sphalerite (average size 1.5 by 1.5 cm and 0.5 to 1 mm thickness) showing transmittance values greater than 50 pct in the 1,300- to 900-cm^{-1} frequency range were chosen for these studies. Santander sphalerite plates were very pale yellow, with occasional darker, almost orange, bands. Plates of Mexican sphalerite were pale green; those of Balmat sphalerite were reddish brown and less transparent.

METAL ION ACTIVATION AND XANTHATION

Plates of sphalerite were immersed in 25 mL of a 5×10^{-3}M $CuSO_4 \cdot 5H_2O$ solution at pH 4.5 for 30 min. This pH was chosen to avoid any precipitation of copper hydroxo species, the pH was adjusted with NaOH or H_2SO_4 solutions rather than using a buffered system which could introduce additional spectral features and/or react with Cu(II). After activation, the plates were removed from the solution, rinsed several times with water, and vacuum-dried. The infrared spectra of the plates were checked for residual sulfate bands (1,200- to 1,000-cm^{-1} region) from the activating solution to ensure that no copper sulfate film was left on the surface.

Two methods of xanthation were employed. One method consisted of immersing the activated plates in the xanthate solution (1×10^{-3}M) for 30 min. After xanthation, the plates were removed from the solution, rinsed with water, and allowed to dry. Spectra were obtained approximately 3 min after the water rinsing.

The in situ method consisted of compressing a small drop of the xanthate solution (1×10^{-3}M) between two sphalerite plates in the demountable cell, placing the cell in the beam compartment, and collecting spectra at set time intervals. In situ measurements were performed with plates of Santander sphalerite.

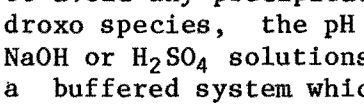
Experiments using Pb(II) as the activating metal ion were performed following the same methods described above (unless otherwise specified), but using a $Pb(NO_3)_2$ solution and Santander sphalerite plates.

REAGENTS

All reagents were reagent grade, and water was deionized (18 MΩ). Potassium ethylxanthate (Eastman) was recrystallized three times by dissolving the material in acetone followed by reprecipitation with petroleum ether. After filtration, the solid was washed several times with diethylether and stored in tight jars. Small portions of the recrystallized material were washed with diethylether prior to use.

Copper, lead, and zinc ethylxanthates were obtained by precipitation from solutions of the corresponding metal salts ($CuSO_4 \cdot 5H_2O$, $Pb(NO_3)_2$, and $ZnSO_4 \cdot 7H_2O$, respectively) with potassium ethylxanthate.

Diethyldixanthogen,



$CH_3CH_2-O-C(=S)-S-S-C(=S)-O-CH_2CH_3$, was prepared by slowly adding 10 mL of a solution containing 1×10^{-3} mol potassium peroxydisulfate to 20 mL of a solution containing 2×10^{-3} mol potassium ethylxanthate. The reaction mixture was allowed to rest 10 min. The milky-looking mixture was centrifuged to separate the oily, yellow dixanthogen. The oily product was washed several times with water (followed by centrifugation after each washing) to remove any unreacted material. The

dixanthogen was pipetted, and a drop was placed between NaCL or KBr windows. Another portion of the oily product was dissolved in diethylether and allowed to evaporate on an NaCl or KBr window. The spectra recorded on samples prepared by the two techniques were consistent with the spectrum of diethyldixanthogen reported in the literature (19-21).

RESULTS AND DISCUSSION

The infrared spectrum of an aqueous solution of potassium ethylxanthate (1×10^{-3}M) contained between two sphalerite plates is shown in figure 3*A* together with the spectrum of solid potassium ethylxanthate in a KBr pellet (fig. 3*B*). The broadening of bands and disappearance of spectral features, as well as changes in the relative intensities of the peaks in the solution spectrum when compared to the spectra of the solid, is typical of the spectra of solutes in solvents. It is caused by solute-solvent interactions and by the averaging of preferred molecular orientations in the solvent medium. The spectrum in aqueous solution is similar in shape to that reported by Poling and coworkers (15-16) for a liquid film. In the present work, the absorption peaks are found at higher energies (1,045 cm^{-1} and 1,118 cm^{-1}) than those reported by Poling and coworkers (1,040 cm^{-1} and 1,111 cm^{-1}), while the broad 1,160-cm^{-1} band they observed is split into two peaks at 1,176 cm^{-1} and 1,148 cm^{-1} in the spectrum in figure 3*B*. These differences may be due to instrument calibration, resolution, sampling techniques, or concentration effects.

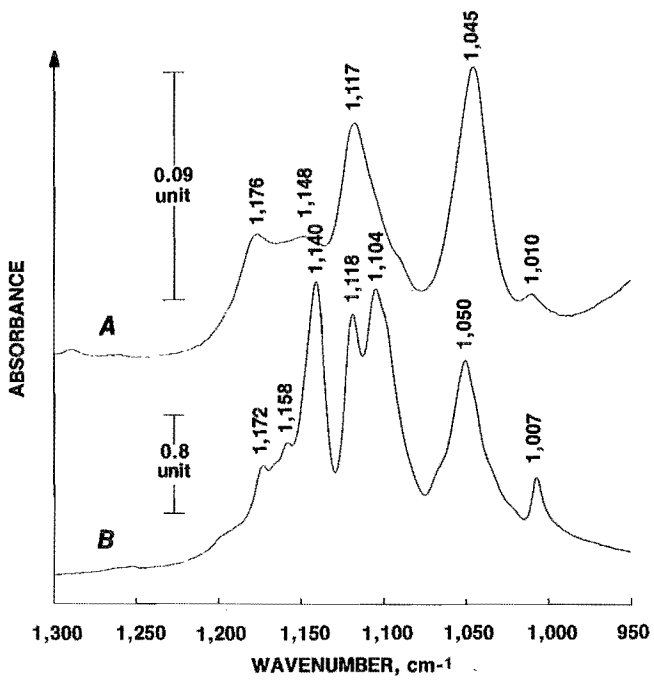


FIGURE 3. - Vibrational spectra of potassium ethylxanthate. *A*, In aqueous solution between ZnS windows; *B*, solid in a KBr pellet.

The infrared spectrum of diethyldixanthogen (neat oil between KBr windows) is shown in figure 4*A* and is consistent with the spectrum reported by Leja, Little, and Poling (19-20) and by Shankaranarayana and Patel (21). The low-energy region (fig. 4*B*) showed distinct bands at 529 cm^{-1} and 378 cm^{-1}, which are not present in the spectrum of potassium ethylxanthate. Compounds containing a disulfide group (that is, an S-S bond) have stretching S-S bands in this region (22); thus, these bands can be associated with the S-S bond in dixanthogen.

Figure 5*A* shows the spectrum of freshly precipitated copper ethylxanthate. It is well known that dissolved Cu(II) salts can oxidize xanthate anions to dixanthogen (23). Dixanthogen-related bands are evident in the 1,200- to 1,300-cm^{-1} region and at 1,022 cm^{-1}, together with the copper ethylxanthate bands. Figure 5*B* shows the solid after several washings with diethylether to remove dixanthogen, and figure 5*C* is a subtraction of spectrum 5*B* from spectrum 5*A*, which essentially leaves the spectrum of dixanthogen shown earlier in figure 4*A*. In comparing spectrum 5*B* (copper ethylxanthate) with that of solid potassium ethylxanthate (fig. 3B), distinct bands at 1,197 cm^{-1}, 1,122 cm^{-1}, and 1,034 cm^{-1} can be noticed in the spectrum of copper ethylxanthate. Based on the results of Hunt, Krüger, Smith, and Winter (24) for other metal xanthates, the bands at 1,197 cm^{-1} and 1,034 cm^{-1} can be attributed to C-O and C-S vibrations, respectively, while weaker bands at 450 cm^{-1} and 351 cm^{-1}

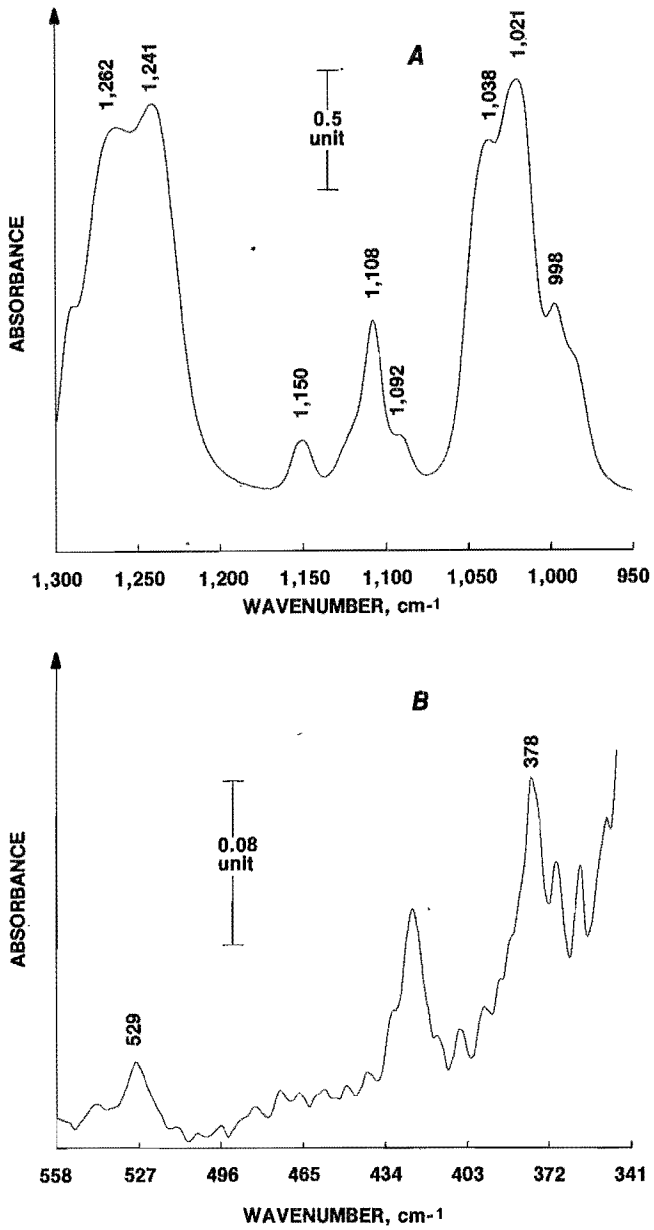


FIGURE 4. - Vibrational spectrum of diethyldixanthogen (Neat oil between KBr windows). *A*, 1,300 to 950 cm^{-1} region; *B*, lower energy region.

(fig. 6) are likely to be associated with Cu-S vibrations. Because ZnS is strongly absorbing below 800 cm^{-1}, it was not possible to use the weaker, low-frequency bands to identify metal-sulfur bonds on sphalerite surfaces. The copper xanthate has been identified as a copper(I) ethylxanthate species (16, 20, 23), but to date no molecular structure for this compound has been reported. The spectrum of zinc ethylxanthate is shown in figure 7, for comparison with the copper species.

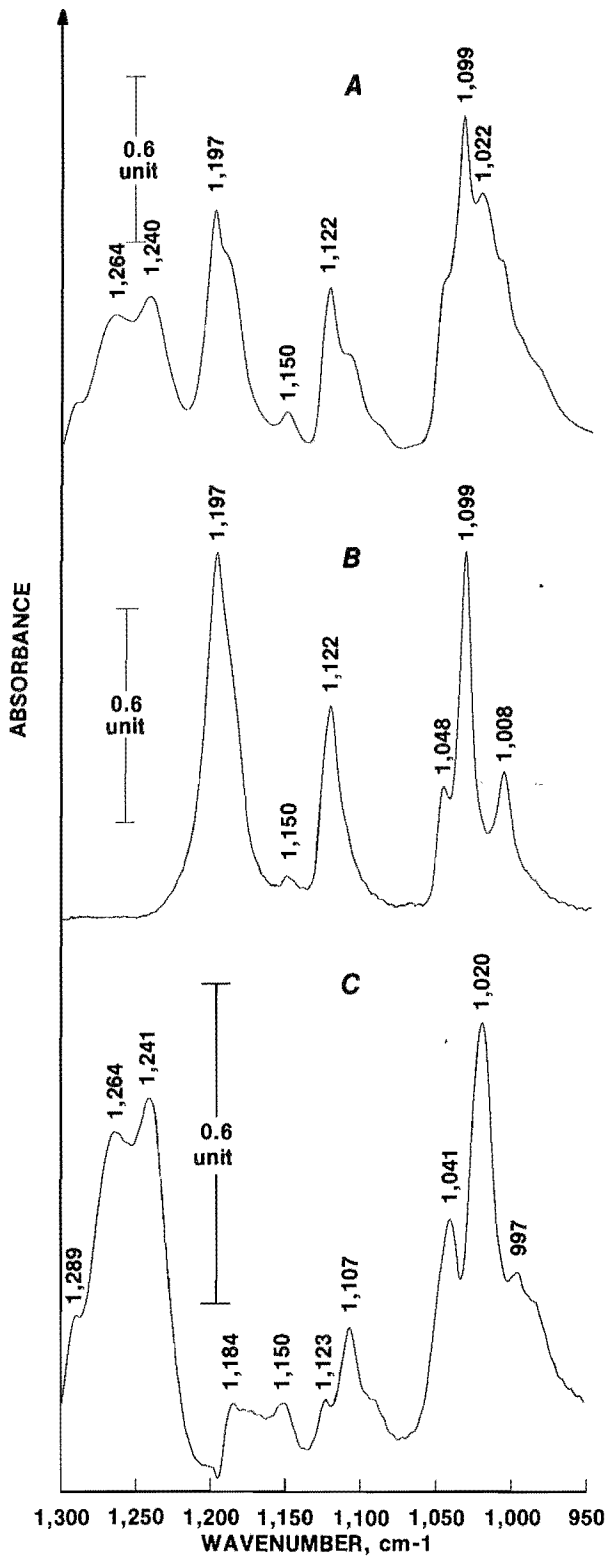


FIGURE 5. - Vibrational spectra of copper ethylxanthate. *A*, Freshly precipitated product; *B*, after washing with diethylether to obtain pure copper(I) ethylxanthate; *C*, a subtraction of spectrum *B* from *A* showing that the removed product was diethyldixanthogen. All spectra were recorded as KBr pellets.

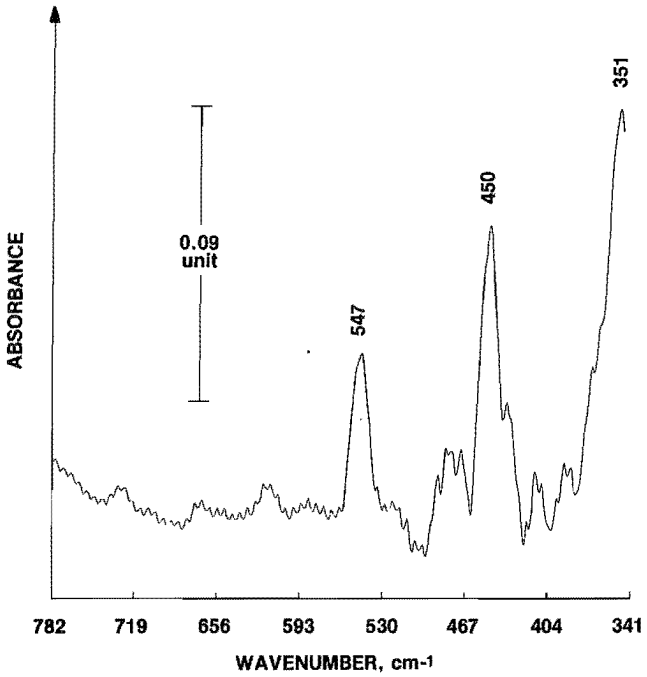


FIGURE 6. - Vibrational spectrum of copper ethylxanthate in the lower energy region.

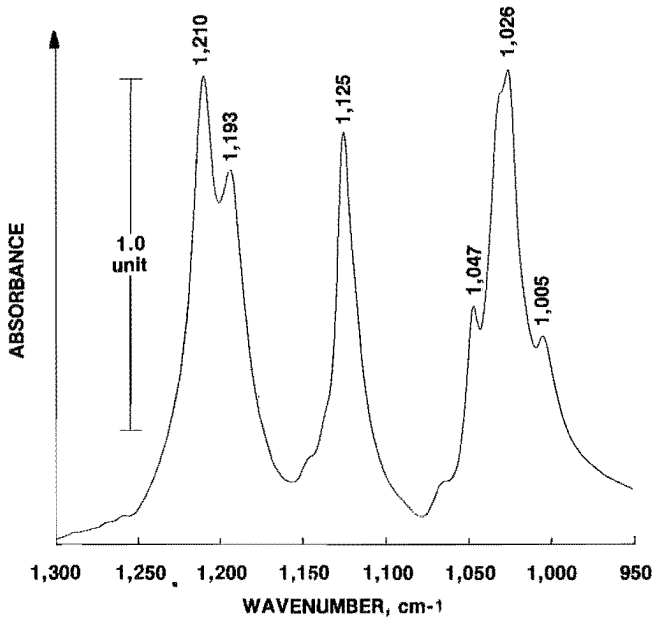


FIGURE 7. - Vibrational spectrum of zinc ethylxanthate. Solid in a KBr pellet.

When plates of copper(II)-activated sphalerite were immersed in the xanthate solution, rinsed and air-dried, the spectrum in figure 8 showed the presence of copper ethylxanthate on the surface. No bands associated with zinc ethylxanthate were observed in either unactivated or activated sphalerite.

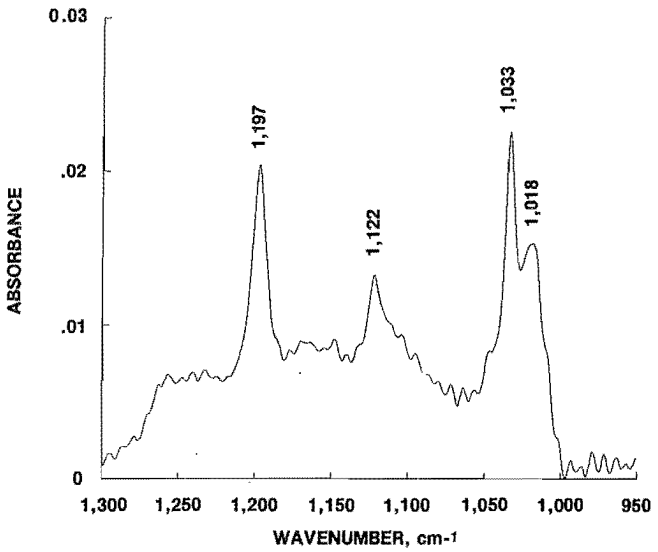


FIGURE 8. - Spectrum of Cu(II)-activated, xanthated sphalerite after drying (immersion method).

X-ray photoelectron spectroscopy (XPS) was used to verify that the copper after activation was actually in the lattice, and not a residual film from the activating $CuSO_4 \cdot 5H_2O$ solution. XPS established that there was no sulfate sulfur on the surface and that the copper was present on the surface lattice as a Cu(I) species. Unactivated sphalerite surfaces gave large charging effects (insulating), while the activated surfaces exhibited negligible charging, as would be expected for a conducting Cu(I) sulfide surface. XPS experiments by Perry, Tsao, and Taylor (25) have suggested that this Cu(I) sulfide is chalcocite.

It was also found that the infrared spectral features of a freshly xanthated surface disappeared with time and were no longer present after a week of exposure to air. The disappearance of infrared spectral features was even more marked when the plates were placed in the vacuum chamber of the XPS spectrometer. A similar effect has been reported by Poling and Leja (15), who found that adsorbed multilayers of bulk-like lead ethylxanthate desorbed from surfaces when subjected to high vacuum for a few days, leaving a near-monolayer thickness of lead ethylxanthate. All these examples

indicate that treated surfaces can undergo further changes once they have been removed from the reacting medium. Therefore, care should be exerted when interpreting results from ex situ experimental techniques, in particular those involving high-vacuum conditions.

Spectra during reaction of Cu(II)-activated sphalerite over a 45-min period are shown in figure 9. Characteristic copper ethylxanthate bands at 1,197 cm^{-1}, 1,120 cm^{-1}, and 1,034 cm^{-1} (compare with spectrum 5*A*) were already present after 5 min of reaction, and continued to grow as the reaction proceeded. After 45 min, the plates were separated, rinsed well with water, and air-dried. Spectra of the plates immediately after drying (about 3 min) also showed the characteristic bands of copper ethylxanthate (fig. 10). When nonactivated plates were used, no changes in the spectrum of aqueous potassium ethylxanthate solutions were observed during the 45-min period and no xanthate-related bands were found after drying the plates.

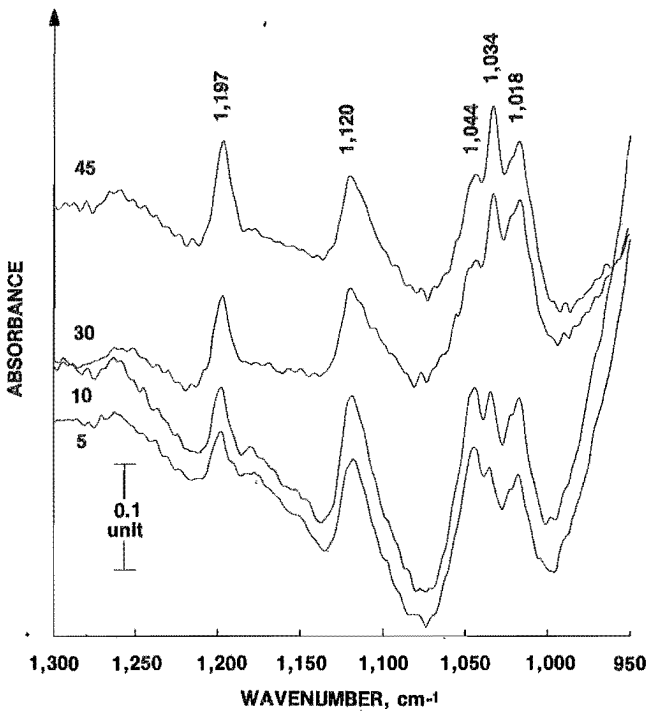


FIGURE 9. - Spectra of an aqueous solution of potassium ethylxanthate during in situ reaction with Cu(II)-activated sphalerite as a function of reaction time, in minutes.

The product formed in the reaction between Cu(II)-activated sphalerite and potassium ethylxanthate solution was mainly copper (I) ethylxanthate, although traces of dixanthogen can be observed in the spectra on figure 9. These results are consistent with those reported by others on Cu-activated sphalerite (12-13) and on copper surfaces (15-16). It was possible that dixanthogen could have formed in solution by reaction with atmospheric oxygen since no attempts were made to exclude air. Yellow, oily droplets of dixanthogen could be observed in aged xanthate solutions exposed to air; the spectra of plates immersed in these old solutions confirmed the presence of dixanthogen. The dixanthogen appeared to be physically adsorbed since it was readily removed with diethylether; similar results were observed by Coleman, Powell, and Cochran (13). The larger amount of dixanthogen they detected was probably due to longer contact times (2 h) with xanthate solutions. A long activation time (90 min) did not increase the production of dixanthogen.

Dry Cu(II)-activated and xanthated plates of the three types of sphalerite studied showed the characteristic copper ethylxanthate bands. Balmat sphalerite plates exhibited new bands at 4,534 cm^{-1}

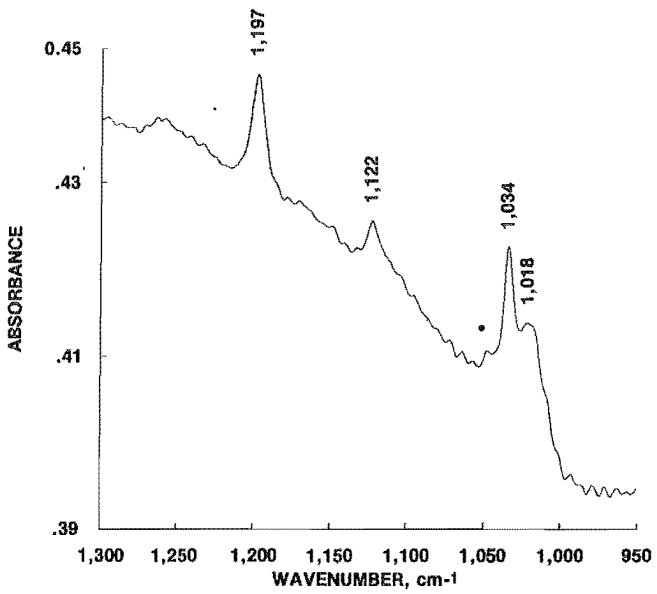


FIGURE 10. - Spectrum of Cu(II)-activated, xanthated sphalerite after drying (after in situ reaction).

and 2,578 cm^{-1} after copper activation, but it was not possible to correlate these bands with any copper-related chromophore.

Figure 11 shows the in situ reaction of Pb(II)-activated sphalerite plates with 1×10^{-3}M potassium ethylxanthate solution. Bands at 1,045 cm^{-1}, 1,118 cm^{-1}, and 1,179 cm^{-1} are likely to be related to those of potassium ethylxanthate in solution (fig. 3A). However, the 1,010 cm^{-1} band in the potassium ethylxanthate solution between unactivated sphalerite plates shifted to 1,018 in Pb(II)-activated plates, suggesting that this band could be related

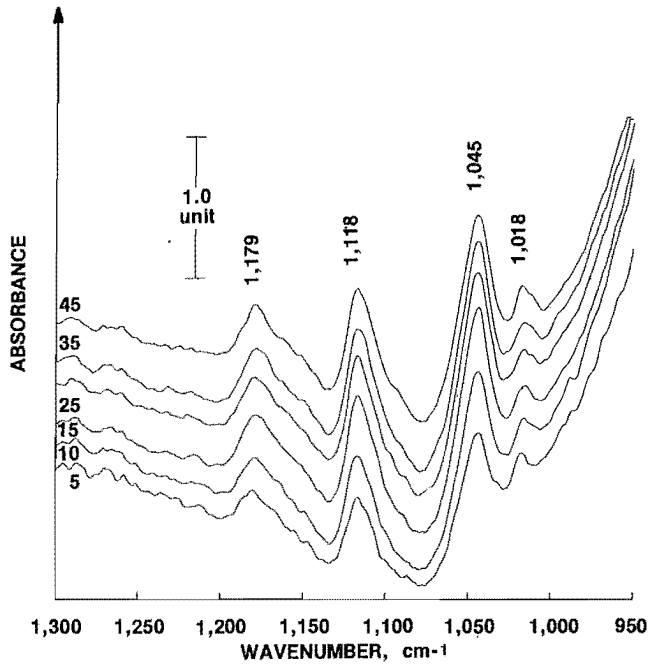


FIGURE 11. - Spectra of an aqueous solution of potassium ethylxanthate during in situ reaction with Pb(II)-activated sphalerite as a function of reaction time, in minutes.

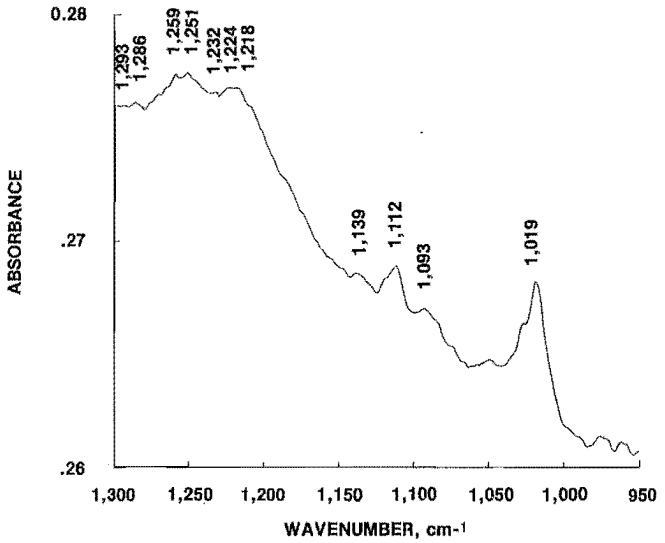


FIGURE 12. - Spectrum of Pb(II)-activated, xanthated sphalerite after drying (after in situ reaction).

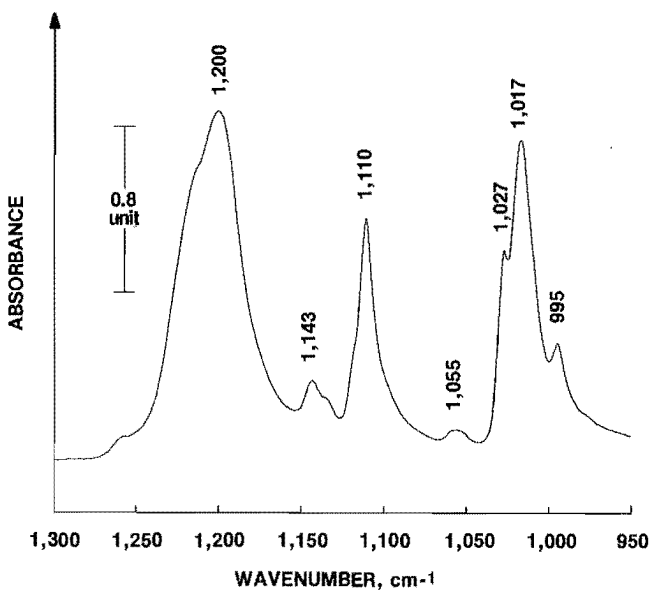


FIGURE 13. - Vibrational spectrum of lead ethylxanthate. Solid in a KBr pellet.

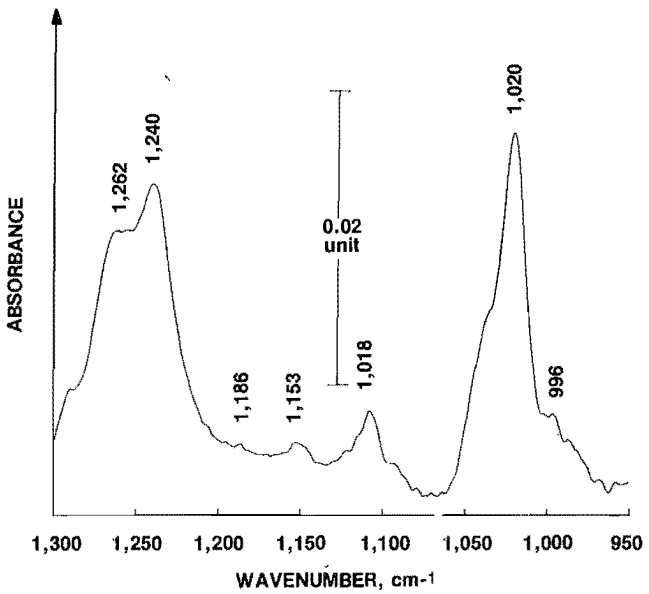


FIGURE 14. - Spectrum of Pb(II)-activated, xanthated sphalerite after drying (activation time 90 min).

to a species other than aqueous ethylxanthate. Dry plates were characterized by strong absorption bands at 1,109 cm^{-1} and 1,112 cm-1 (fig. 12). Comparison with the spectrum of lead ethylxanthate (fig. 13) suggested the presence of a lead ethylxanthate species on the surface, although the broad 1,200-cm^{-1} band is not as well defined as it is in the spectrum of bulk lead ethylxanthate. The bands between 1,251-1,259 cm^{-1} and 1,286-1,293 cm^{-1} suggest traces of dixanthogen.

For sphalerite plates activated with Pb(II) for 90 min and then reacted with xanthate for 30 min, the spectrum (fig. 14) is characteristic of dixanthogen, as evidenced by the bands in the 1,300- to 1,200-cm^{-1} region and in the vicinity of 1,020 cm^{-1}. Because the concentrations of xanthate and the reaction times were the same for both 30- and 90-min activation times, the predominance of dixanthogen as a reaction product at longer activation periods suggests that surfaces richer in Pb (and which are perhaps more PbS-like) favor dixanthogen formation, possibly owing to a catalytic effect of the Pb-enriched surface. Adsorbed xanthate in a one-to-one coordination with lead, bulk lead xanthate, and dixanthogen have all been reported as products of galena-xanthate reactions (26).

CONCLUSIONS

It has been shown that FT-IR by a transmittance method can be used to follow, in situ, the reactions of aqueous solutions of potassium ethylxanthate with Cu(II)- and Pb(II)-activated sphalerite. Polished sphalerite plates served as both the reacting mineral surfaces and the infrared-transparent windows.

Activation with Cu(II) ions led to a Cu(I) sulfide-like surface, which reacted with potassium ethylxanthate to form copper(I) ethylxanthate on the surface.

With Pb(II)-activated sphalerite, the surface products depended on the length of activation. Samples activated for 30 min yielded a lead ethylxanthate-like product, while samples activated for 90 min yielded dixanthogen. The latter may be due to a catalytic effect of the richer Pb (and more PbS-like) surface.

No evidence for formation of zinc ethylxanthate was found with either unactivated or activated sphalerite plates.

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